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# AUTOMATIC DEVICE FOR DENSITY MEASUREMENT IN POLYETHYLENE

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## INTRODUCTION

Polyethylene, be it low density (LDPE) or high density (HDPE) is one of the most important, if not the most important product of the plastics industry. As it is the case for all industrial materials, it is of primary importance for the manufacturer and the processor to have means of characterizing the material.

From a somewhat simplistic point of view, polyethylene can be considered as a binary mixture of an amorphous and a crystal phase and the degree of crystallinity will affect the elastic properties (elastic modulus, impact strength and melting point). On the other hand, it is known [1] that density is directly related to the degree of crystallinity: so that in the relationship between the basic parameters of P.E. and its end properties, the value of density is an important link. This explains why the value of density has always been the major criterion for the characterization of polyethylene.

The most commonly used and accepted method for the determination of density is that of the "Density Gradient Column" defined by ASTM D1505 standard [2]. The sample is placed in a column of liquid which exhibits a known density gradient; after the sample has sunk to its equilibrium, the density is obtained from the reading of its position in the column.

As such, the procedure appears to be simple but it is in fact quite involved. First, the column must be prepared from a mixture of different solutions of known densities. This is time consuming, requires much care at all stages and is much of an art. The column which is placed in a constant temperature environment is then calibrated, using standard glass floats (the calibration has to be verified periodically). To perform the measurement, the samples are cut to size, cleaned, wetted down and gently introduced in the column where they settle in roughly 20 minutes. When after a number of measurements the number of samples in the column is too important they must be retreived carefully with a basket, without upsetting the gradient.

Here we propose a method and technique based on the propagation of ultrasound which allows for an accurate and reliable determination of density. The technique is simple and can be used in an uncontrolled environment; the measurement is quick and can be made automatic.

## I. EXPERIMENTAL METHOD

For a number of polymers, the ultrasonic data are available from the literature [3]; sparse results are found for the sound velocity and density [4,5]. The special case of polyethylene has, however, been given closer attention [6,7,8,9] and the various results tend to show that there exists a correlation between sound velocity (v) and density ($\rho$).

The most complete and conclusive study is that of Davidse et al [7]. They have measured, using a resonance method, the propagation velocity of low frequency oscillations (5 to 10 kHz) in bars of P.E. and their results on a great number of samples show that the velocity is proportional to the density. The technique they have used is involved: it requires preparation of samples and the determination of velocity takes into account geometrical effects and on a priori knowledge of the Poisson ratio for the material.

It is our objective here to verify the existence of a possible correlation between the velocity and the density, to describe the correlation and to propose a technique by which the velocity can be obtained in a rapid yet precise way so as to allow for the determination of density.

In our study, we use an immersion technique [4,10] because of the ease with which the measurements can be made and repeated. The principle of the method where a single transducer is used as both the emitter and the receiver is illustrated in Fig. 1. A high frequency (MHz) sound pulse S travels with a normal incidence onto the sample (a plate of thickness d). There it sees part of its energy reflected back ($E_1$) and reaching the transducer at time $t_1$, and part of it going through the sample where it later meets the second interface: again part of the energy is reflected, part is transmitted and so on. This gives rise to the formation of echos ($E_1$, $E_2$...) which are seen at times $t_1 + \tau$, $t_1 + 2\tau$ ... ($\tau$ is the time for the sound to travel back and forth in the sample). If v is the velocity of sound in the sample, then

$$\tau = 2d/v$$

In order to obtain v, one needs to know the value of d with sufficient precision so as to obtain the required accuracy. This measurement could be made using a micrometer but this would be both annoying and not very accurate. The samples being rough from press show surface and thickness irregularities so that the value of d must be some average taken at the location of insonification. We have chosen to take the thickness into account through acoustics. Part of the energy after having traversed the sample is transmitted forward in the liquid. This signal can be reflected back to the transducer by use of an acoustic reflector M. If $t'_1$ is the time it takes the sound pulse to go from the sample to the mirror and back, a signal will be detected at time

$$t' = t_1 + \tau + t'_1 = t_1 + 2d/v + t'_1$$

The sample being removed, the signal coming from the mirror appears at time

$$t'' = t_1 + 2d/c + t'_1$$

where c is the velocity of sound in the liquid.

Considering the difference in the times of flight yields

$$t' - t'' = \Delta t = 2d\ (1/c - 1/v)$$

This together with the expression of $\tau$ gives

$$v = c\ (\Delta t/\tau + 1)$$

Thus, from the sole measurement of time delays, and the knowledge of c, one obtains the value of the velocity of sound in the sample.

## II. EXPERIMENTAL PROCEDURE AND RESULTS

The samples (50) corresponding to a broad range of densities were furnished by DuPont Canada. They were in the form of press molded plaques (80 X 50 X 1.9 mm) prepared according to ASTM standards from a variety of commercial grades of P.E. In the measurements, they were used as is with no preparation. A number of pieces (2 to 4) were cut from the plaques and their density measured in a density gradient column following the standard ASTM procedure. This was done once before the velocity measurements were performed and repeated afterward. The values are given with an accuracy of $\pm$ .0008 g/cm$^3$ at a constant temperature t = 23°C.

The ultrasonic set up was designed to accomodate such samples and placed in a bath of demineralized water at 23°C. The transducer is of the commercially available immersion type. In order for the echos to be well separated in time, the pulses must be short: this calls for a highly dampened transducer operating at high frequency. However, the attenuation of sound in P.E. rapidly increases with frequency and this sets an upper limit. We found that 3MHz constitutes a good compromise between time resolution and signal amplitude. The reflector, located roughly 15 cm from the transducer, is a flat piece of glass with an absorbant backing so that no signals (echos) are issued other than the reflexion from the front face. The set up is rather simple and the only requirement is that the samples and reflector be perpendicular to the sound beam.

Concerning the electronics, we used a Metrotec pulser (Mod. MP 203) capable of delivering short (100 n sec) high voltage (300 volts) pulses with a repetition rate of 50 to 100 Hz. The receiving amplifier was also Metrotec (Mod. MR 101) with a 60 dB gain factor and a 20 MHz band width. The RF signal is monitored on an oscilloscope (H.P. Mod. 1743A) which is equipped with a dual time base that allows time delay measurements with an adequate resolution (3 n sec or better).

First, the sound velocity in the water has to be measured: this is accomplished by displacing the reflector by a known distance and noting the arrival times. We obtain a value of $c = (1.483 \pm 0.001) \times 10^5$ cm/sec at 23°C, in good agreement with what is found in the literature from which we quote the temperature dependence: 200 cm/sec°C.

The results for our measurements of sound velocity (at 3 MHz) in polyethylene samples of different densities are illustrated in Fig. 2. To a good approximation, the velocity is proportional to density and, performing a linear regression analysis of our data yields $v = a\rho + b$ with $a = 10.16 \times 10^5$ cm$^4$/sec g, $b = -7.40 \times 10^5$ cm/sec and a correlation factor $r = .9935$.

In turn, considering the relation from which the velocity is calculated and given the various instrumental errors, we can estimate the experimental uncertainty as $(\delta v/v)$ inst = $\pm$ .0012. Such an accuracy, which corresponds to an upper limit for velocity measurements, is only made possible by the fact that the thickness is taken into account acoustically. For an average value $v = 2.5 \times 10^5$ cm/sec, we find $(\delta v)$ inst = $\pm$ 300 cm/sec and $(\delta \rho)$ inst = $\pm$ .0004 g/cm$^3$. The added effect of temperature fluctuations yields ($\delta v$ temp = $\pm$ 500 cm/sec°C or $(\delta \rho)$ temp = $\pm$ .0005 g/cm$^3$ °C.

In practice, for a given plaque the spread in the values obtained at different measuring points is somewhat larger (by a factor of 2). Our observations, using transducers of increasingly larger diameters (.2 cm for a focused beam up to 4 cm) show that the scatter becomes less. This amounts to measuring a value of velocity which is averaged over a wider area. When repeating the measuremnt at the same location on the plaque, the resulting value is constant within $\delta v$ = $\pm$ 300 cm/sec. This tends to show that the inhomogeneity in the density of the plaque is the main source of uncertainty. We found that with a transducer having a beam width of 1 cm ($\frac{1}{2}$ in.) the spread becomes comparable to what is obtained from the density column ($\delta \rho$ = $\pm$ .001 g/cm$^3$). To stay within this range, the allowable fluctuations of temperature will be = $\pm$ 3°C, which is easily attainable in a normal air-conditionned room.

## CONCLUSION

We have demonstrated that in commercial grades of polyethylene, there exists a linear relationship between the sound velocity at ultrasonic frequencies and the density of the material. We have shown experimentally that the velocity measurements can be performed with sufficient accuracy to allow the computation of density. The method we describe is simple; and since it is based on the sole measurement of time delays, it can be made automatic through digitalization. The advantages of the method are numerous when compared to the classical density

gradient column: a) no preliminary preparation, the set up is completely portable, suffers little influence from the environment and requires no special care to upkeep, b) the sample is not destructed and can be kept for files, c) the measurement is fast, reliable and repeatable, the accuracy is good ($\delta\rho = \pm .001$ g/cm$^3$) and the operation being simple requires no special attention, care nor skill.

Further work is needed to check whether such a technique could be applicable to other polymers and also to examine the influence of fillers (silica, carbon black...). Further work is also needed in order to establish the physical foundation for the observed behaviour.

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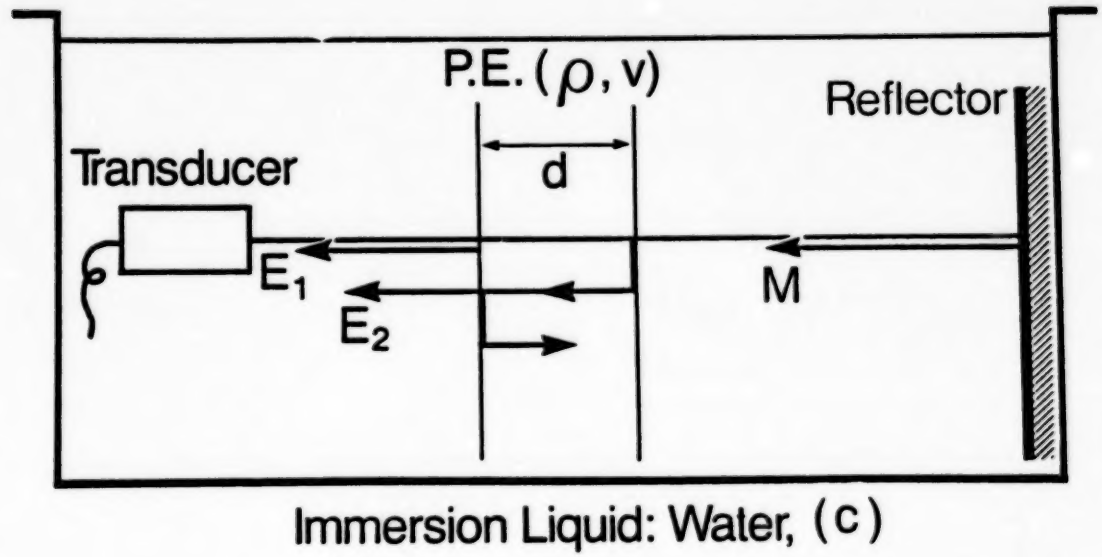


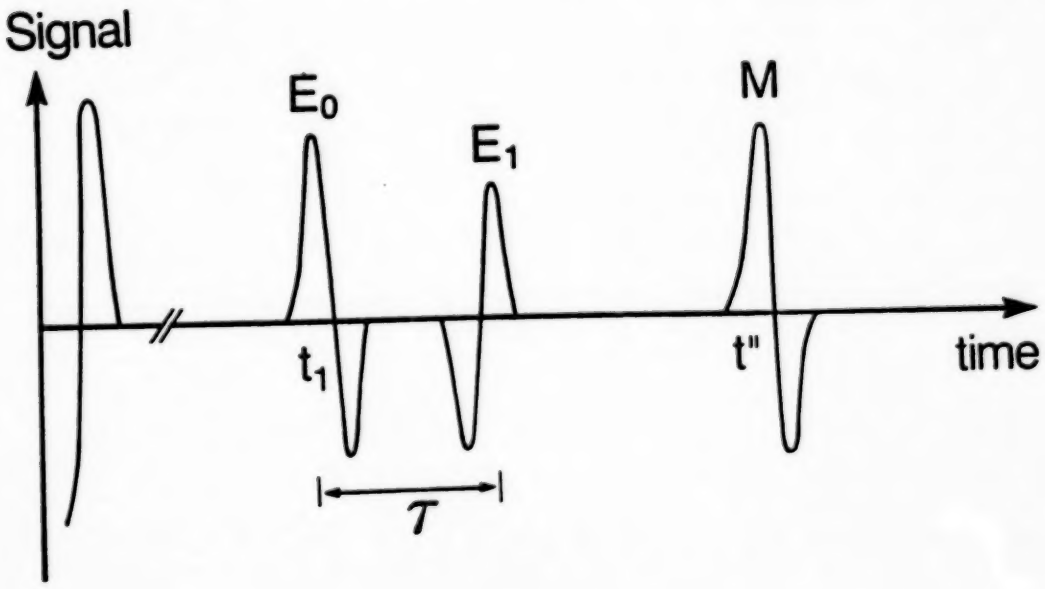


Figure 1: a) Schematic description fo the path followed by the sound beam as it travels through the water and interacts with the sample; b) representation of the different signals which are to be observed on an oscilloscope.

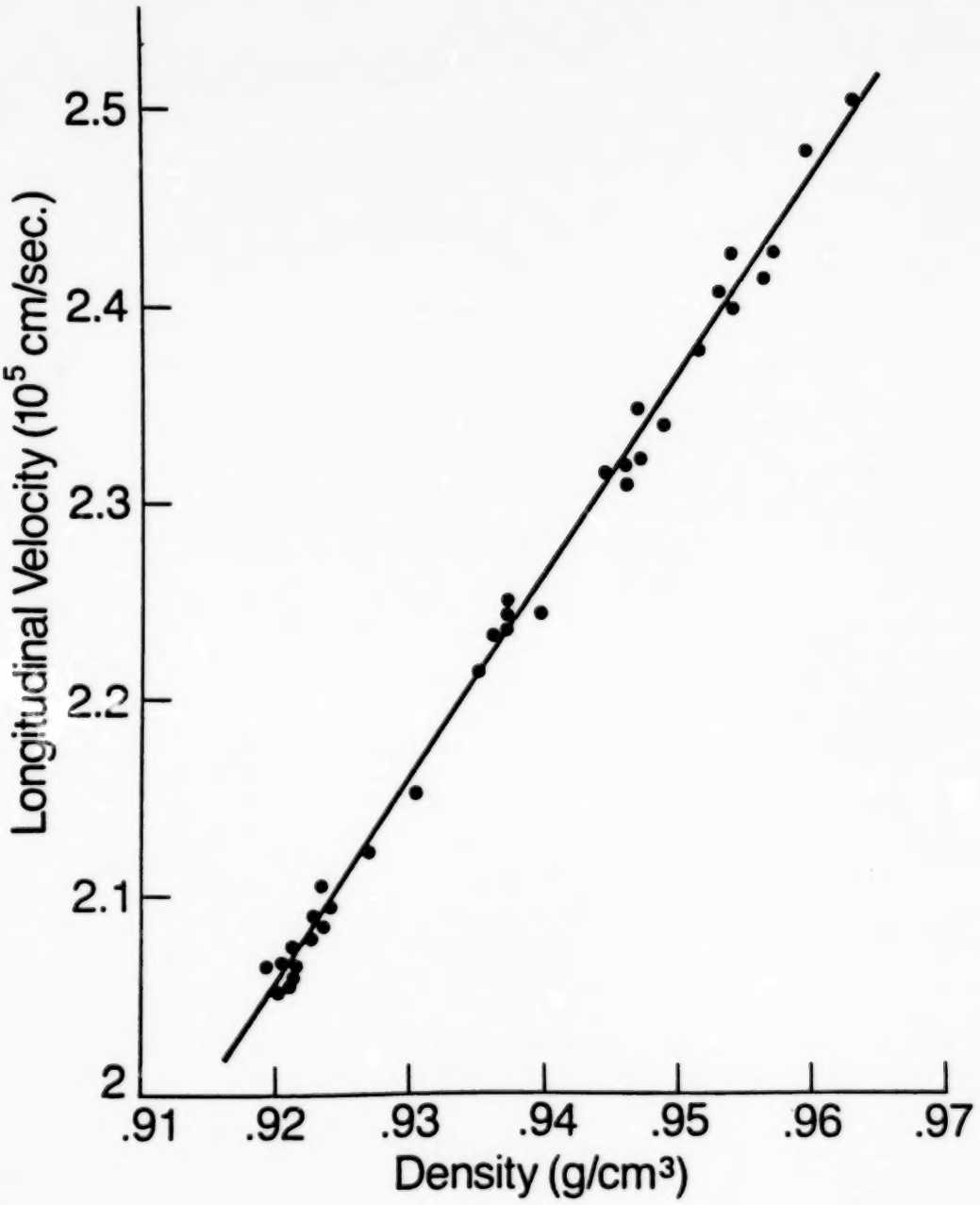


Figure 2: Results obtained for the measurement of ultrasonic (3 MHz) sound velocity in plaque samples of commercial grade polyethylene, the density of which was measured in a density gradient column at 23°C.